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OPTIMUM RATIO OF CATIONS ON NUCLEAR SULFONIC ACID RESIN FOR MINIMUM CHANGE IN COMPOSITION OF RESIN-TREATED MILK

SUMMARY

The optimum mole fraction of the major cations (Ca^{++}, K^{+}, Na^{+}, and Mg^{++}) on a strong sulfonic acid ion exchange resin for minimum change in milk composition was determined by equilibrating the resin with milk at pH 5.4 and 6.6. The fraction of calcium on the resin increases with decreasing pH, whereas those of sodium and potassium decrease. Since magnesium is present in relatively small amounts, it appears to be little affected by pH, possibly due to experimental error involved in its determination.

By using the milk-equilibrated mole fraction of the cations on the resin, and the apparent equilibrium constants involving these ions and the resin, mixed regenerating solutions of the chlorides of the four cations were prepared. The concentrations were adjusted so that the ratio of ions on the resin would be in equilibrium for milk at pH 6.6 and 5.4. Milk passed through columns of these resins showed little change in the cationic composition.

The cationic composition of milk varies with breed of the animal, season of the year, and with other factors. Consequently, the milk-equilibrated mole fraction of cations placed on a resin will vary. The effect of this variability of changes required in the regenerant composition is the subject of a current study.

Several laboratory studies have been reported recently for removing radioactive strontium from milk by use of ion exchange techniques (1, 2, 7, 9). Most of the work has been done with nuclear sulfonic acid resins, e.g., Dowex 50 or Amberlite IR-120. It is highly desirable in this treatment, in addition to removing the strontium, to obtain milk with as little change in the cations as possible. Small changes in the mineral balance may affect the physical stability during subsequent processing. Treatment of milk with a single ion-saturated resin, such as calcium or sodium, results in marked changes in the cationic composition. Migicovsky (7) used Dowex 50W resins charged with a mixed solution of the chlorides of calcium, potassium, and sodium, in which the proportions of the cations were the same as in milk. He reported no significant change in the content of the three cations studied when milk was contacted with the resin in batch form and at the normal pH of milk. These results may be expected for small resin-to-milk ratios, even though the cations on the resin are not in equilibrium with the cations in the milk. This might also be expected when analyses are made on milk obtained from a column experiment if a large volume of effluent milk were pooled. However, significant changes may be obtained in the cationic composition from the first few bed volumes of effluent from an improperly charged column (4).

Under proper conditions exchange reactions are perfectly reversible with modern exchange resins. By washing a resin with an excess of an electrolyte it can generally be converted wholly into the required salt form. Thus, in the reaction:

$$\mathrm{Na\,R} + \mathrm{K^{+}(aq)} \rightleftarrows \mathrm{KR} + \mathrm{Na^{+}(aq)} \qquad (1)$$

where R represents a cationic exchange resin, Na^{+} can be completely displaced from the resin by potassium ions if the sodium ions are continually removed as they are released. With milk this means that the strontium ions can be replaced from the milk by sodium, potassium, magnesium, or calcium ions. If, however, a quantity of NaR is brought into contact with a solution containing both sodium and potassium ions, an equilibrium is eventually established for Eq. (1), and the position is reproducible and independent of the side from which it is approached. The exchange is necessarily equivalent. The position of equilibrium de-

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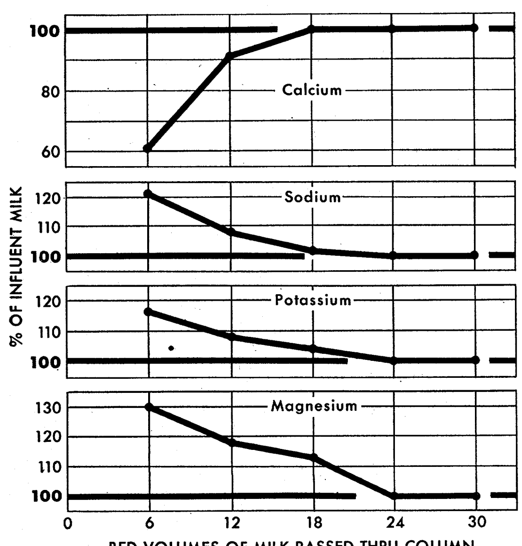
pends, of course, on the relative proportions of K^+ and Na^+ in solution, on the chemical nature of other ions or complexes present in the solution, and on the nature of the resin employed. The relative affinity of the ions for the resin are $Sr^{++} > Ca^{++} > Mg^{++} > K^+ > Na^+$.

Milk will not behave as a simple salt solution for several reasons. Milk is a colloidal system and contains a great many ligands capable of complexing with divalent ions. The position of the equilibrium with the resin will depend on the different equilibria in milk which are affected by the pH and temperature. The heterogeneous nature of some of the equilibria with divalent ions makes the system more complicated than an aqueous solution containing anions having the ability to act as ligands, that is, coordinating ions or molecules. The major cations in milk are Na^+, K^+, Ca^{++}, and Mg^{++}. The alkaline earth metals form complexes with a great many of the anions in milk, e.g., with citrate, phosphates, proteins, and minor constituents. Therefore, the total analytical composition of milk cations will not be a measure of the amount capable of exchanging with the resin and is of little value in determining the correct ratio of ions on the resin which will be in equilibrium with the milk.



	Ca	Na	K	Mg
Charging solution* (mM/l.)	312	217	385	43
Resin phase-mole fraction after charging	.370	.087	.474	.070
Control milk–mg./l.	1300	495	1828	117
Mole fraction on resin after equilibration with milk (Avg. of 2 runs)	.531	.069	.343	.056

*concentration equals 10 times normal milk concentration

FIG. 1. Change in the cationic composition of milk after passing through a nonequilibrated resin column (pH of influent milk = 5.4).

Work was undertaken in this laboratory to study the equilibria between a strong acid ion exchange resin (Amberlite IR-120) and the major cations (Ca, K, Na, Mg) in milk. It is shown in this paper that changes in these ions may be minimized, regardless of resin-to-milk ratio, by placing a mole fraction of cations in the resin phase which will be in equilibrium with those in the milk. The equilibria are considered as a function of pH.

The procedure for regenerating the resin with the desired ratio of cations is given in another paper (6). The effect of lowering the pH of milk, before contacting with an ion exchange resin, on the removal of radiostrontium has been reported previously (3, 8).

EXPERIMENTAL PROCEDURE

Reagents and materials. The salts used for charging the ion exchange columns were cp grade chlorides of calcium, potassium, sodium, and magnesium. The ion exchange resin was Amberlite IR-120, having a size range of 16-50 mesh and an exchange capacity of about 2.0 meq/ml of wet resin. Standard solutions for flame photometric analysis of Ca, K, Na, and Mg were obtained from Fisher Scientific Company,[2] as was the EDTA.

Analysis. Analyses for calcium, potassium, sodium, and magnesium were made by flame spectrophotometry as described by Werner (10), using a Beckman Model DU spectrophotometer.[2] The Ca and Mg were also analyzed by Kamal's (5) complexometric procedure.

Preparation and operation of ion exchange columns. Glass columns 21 mm in diameter and 60 cm in length were filled to a height of 30.5 cm with back-washed and settled resin. The salt solutions used to charge the resin were passed downflow at a rate of 0.25 ml/min/ml of resin until equilibrium was attained, and the excess removed with water. After the initial charging, in some experiments, the cations (Ca, K, Na, and Mg) were removed with 6 N HCl and analysis made for the mole fraction. When milk was to be passed through the columns, the resin was first equilibrated with the mixed salt solution as described above and back-washed with water. The milk was passed downflow at 0.25 ml/min/ml of resin. Samples were taken at intervals for determination of the cations. All traces of milk were then removed by washing with water, and the cations

[2] The use of trade names is for the purpose of identification only, and does not imply endorsement of the product or its manufacturer by the U. S. Department of Agriculture.

TABLE 1

Effect of pH on the mole fraction of cations on sulfonic acid resin after equilibration with milk [a]

pH	Calcium	Potassium	Sodium	Magnesium
5.4	0.558	0.329	0.061	0.051
	.534	.341	.069	.052
	.546	.341	.071	0.43
	.573	.321	.059	.046
Average	.553	.333	.065	.048
5.8	0.505	0.369	0.073	0.053
	.490	.382	.075	.053
Average	.498	.376	.074	.053
6.2	0.461	0.405	0.077	0.055
	.432	.423	.085	.065
	.476	.409	.086	.028
Average	.456	.412	.083	.049
6.6	0.440	0.413	0.074	0.063
	.440	.404	.092	.063
	.454	.407	.098	.041
	.422	.408	.104	.058
	.423	.405	.105	.066
	.394	.423	.106	.076
	.451	.420	.100	.028
	.439	.438	.096	.027
Average	.433	.415	.097	.053

[a] Column procedure was used.

again eluted with 6 N HCl to determine the mole fraction on the resin after contact with milk. Acidified milks were prepared by adding 0.5 M citric acid.

The composition of the salt solution varied from one experiment to another, depending on the pH of the milk and whether change in the cationic composition of milk was desired. To obtain milk with no change caused by passage through the resin columns, the composition of the salt solution used to equilibrate the resin was computed by the procedure given in a previous paper (6).

RESULTS AND DISCUSSION

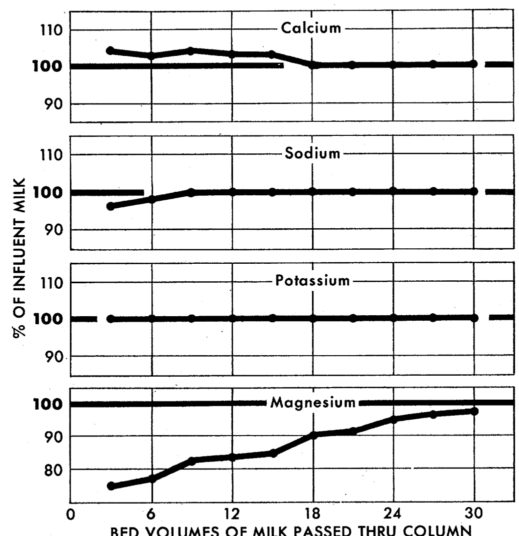
Figure 1 shows the changes in the cations of milk after passing the milk through a resin which had been charged with a solution containing the major milk cations in a ratio similar to the average milk composition. The marked decrease in the calcium, and increases in the sodium and potassium content of the first few bed volumes of effluent milk, reflect the relatively low fraction of calcium on the resin. After sufficient milk had passed through the resin, the effluent composition was equal to the original composition, i.e., a state of equilibrium between milk and resin was attained. The tabulated data accompanying Figure 1 also reveal an initial deficient calcium fraction, and corresponding surplus quantities of sodium, potassium, and magnesium. This is readily seen by comparing the mole fractions on the resin after charging with those after equilibration with milk. The milk in this experiment was adjusted to a pH of 5.4 with citric acid before passing through the resin.

In Table 1 are data from a number of trials showing the mole fractions of the cations on the resin, as a function of pH, after equilibrating with large volumes of milk. The relative amount of calcium obtained on the resin increases with decreasing pH. These data reflect the nature of the complexes formed by alkaline earth metals with organic anions in milk. It is evident that the metal ion acts as a Lewis acid and the ligand as a Lewis base. Because of the basic properties of most ligands they are usually associated with H^+ over a wide pH range. Therefore, the stability of a metal chelate will be a function of pH. In terms of milk this means that the amount of Ca^{++}, Mg^{++}, and Sr^{++} available for exchange should be a function of pH, and at lower pH values more of the ions should be available for exchange, as can be seen for calcium in Table 1. The results for magnesium do not show a trend with pH, possibly because of its relatively low fraction on the resin and because of difficulty in quantitative determination.

Since the mole fraction obtained on the resin varies with the pH of the influent milk, it is necessary to place a different ratio of ions on the resin for milk at different pH values, so that it will be in equilibrium with the resin. The apparent equilibrium constants for the distribution of the milk cations between the resin and aqueous solutions of their chlorides were determined previously (5). Knowing the mole fraction of ions on the resin after equilibration with milk, and the apparent equilibrium constants, the proper concentration of ions in solution which placed the desired mole fraction on the resin was calculated.

These solutions were then used to condition resins at pH 6.6 and 5.4. The mole fraction of these cations in the charging solutions, in the resulting resin phase and in milk at these two pH values, are shown in Table 2. These data show that the concentration of the milk ions at these two pH values differs from that of the calculated optimum charging solution and from that of the resin phase. This is because all of the ions are not available for exchange to the same extent. The relative affinities of the cations (and equilibrium constants) vary with pH, ionic strength, and the nature of other ions or complexes present in the system.

Figures 2 and 3 contain data on the cationic composition of effluent milk when the resin was equilibrated with an optimum ratio of cations for milk at pH 6.6 and 5.4, respectively. The desired (optimum) charge was determined by averaging the mole fractions of ions from several milk-equilibrated resins (see Table 1). The charging solution composition was calculated as described previously (5). Each point on the graphs is the average of two separate experiments. The curves show that the cationic composition of the milk was changed very little after passage through the resin (except for the Mg changes at pH 6.6—Figure 2. Accurate determinations of Mg are more difficult than those of the other cations. Errors in its desired mole fraction would account for the results obtained). Good agreement was obtained



	Ca	Na	K	Mg
Optimum mole fraction	.433	.097	.415	.053
Charging solution (mM/l.)	150	152	331	41.2
Resin phase-mole fraction after charging	.431	.088	.436	.045
Control milk-pH 6.6-mg./l.	1325	481	1844	133
Mole fraction on resin after equilibration with milk (Avg. of 2 runs)	.429	.098	.455	.028

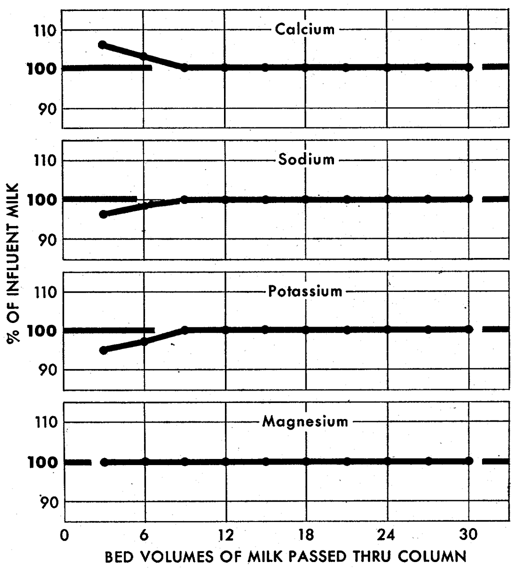
FIG. 2. Cationic composition of effluent milk when resin was equilibrated with optimum charge (pH of influent milk = 6.6).

TABLE 2

Comparison of mole fractions of cations in milk, on equilibrated resin and in solution used to charge resin for optimum charge

pH of milk		Ca	Na	K	Mg
6.6	Milk	.310 (33.1)[a]	.196 (20.9)[a]	.442 (47.1)[a]	.052 (5.54)[a]
	Resin phase	.431	.088	.436	.045
	Charging solution	.233 (150)[a]	.226 (152)[a]	.491 (331)[a]	.060 (41)[a]
5.4	Milk	.312 (28.1)[a]	.203 (18.3)[a]	.440 (39.5)[a]	.045 (4.27)[a]
	Resin phase	.607	.050	.292	.05
	Charging solution	.273 (56.0)[a]	.188 (38.5)[a]	.483 (99.1)[a]	.056 (11.6)[a]

[a] Millimoles/liter.



	Ca	Na	K	Mg
Optimum mole fraction	.553	.067	.333	.048
Charging solution (mM/l.)	56.0	38.5	99.1	11.6
Resin phase-mole fraction after charging	.607	.050	.292	.050
Control milk-pH 5.4-mg/l.	1138	422	1547	103
Mole fraction on resin after equilibration with milk (Avg. of 2 runs)	.580	.060	.306	.054

FIG. 3. Cationic composition of effluent milk when resin was equilibrated with optimum charge (pH of influent milk = 5.4).

between the optimum (desired) mole fractions of cations and the mole fractions on the resin after equilibration with milk. This further confirms that the resins were properly charged.

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